

Vision

Advances in chemical sciences and the resulting technologies allow gaseous CO₂ or its constituent carbon to be transformed into materials that are benign, are inert, are long-lived and contained in the earth or water of our planet, or have commercial value. These transformations represent economical ways to sequester CO₂ or its constituent carbon.

7 ADVANCED CHEMICAL APPROACHES TO SEQUESTRATION

7.1 INTRODUCTION

Advanced chemical processes might lead to unique sequestration technologies or to improvements in our understanding of chemistry that will enhance the performance of other approaches to sequestration. Chemistry is a crosscutting discipline that will interact with virtually all aspects of the sequestration problem. This chapter discusses R&D topics for options not covered in the previous chapters on sequestration technologies but that require advances in our understanding of chemistry.

Advanced chemistry shares significant common ground with separation and capture. Improved methods of separation, transport, and storage will benefit from research into advanced chemical techniques necessary to address sequestration via chemical transformation. Because any sequestration technique will involve storing vast amounts of carbon-rich materials, environmental chemistry is an important cross-linking technology to most of the approaches mentioned in this report. The fate of CO₂ in geological underground storage sites is in part determined by the chemical interaction of the CO₂ with the surrounding matrix, whether it is coal in coal beds or the mineral rock that caps saline aquifers deep underground where brines of carbonic acid can interact. Many issues pertaining to aqueous carbonate/bicarbonate chemistry are relevant to ocean disposal or underground disposal. Carbonate chemistry in very basic solutions may offer potential for extracting CO₂ from air. Because clathrates may be used to separate CO₂ from high-pressure systems, knowledge of their properties may be important to understanding approaches to ocean disposal. Subsurface arctic or

marine hydrate formations may also be evaluated as geologic disposal options. Enhancing soil carbon combines biological and environmental chemistry. Similarly, ocean fertilization generates biomass carbon that may interact with ocean chemistry.

7.1.1 Introduction to the Problem and Solutions

Most anthropogenic emissions of CO₂ result from the combustion of fossil fuels. Advanced technologies are being developed to use fossil fuels for co-production of chemicals along with power, including approaches to decarbonizing methane or coal to produce hydrogen. Hybrid approaches may be developed that are an alternative energy source to create hydrogen, making it reasonable to use the hydrogen and captured CO₂ to produce transportation fuels. A number of web sites contain information on the developmental technologies alluded to. See www.nire.go.jp/NIRE/ and www.fe.gov.doe/coal_power/.

The advanced chemical technologies envisioned for the future would work with the technologies now being developed to convert recovered CO₂ economically to benign, inert, long-lived materials that can be contained in the earth or water of our planet or that have commercial value. Most of the advanced chemical approaches identified in this chapter assume that separation and capture processes will make available pressurized CO₂ with minimal (and defined) impurity levels at ambient temperature (i.e., pipeline CO₂). Decarbonization technologies will produce particulate carbon at the site of the process, while advanced power generation technologies may produce

a separate stream of carbon monoxide (CO) for use as a feedstock at the plant site. Enhanced chemical processes may also play a role in indirect capture of CO₂ via terrestrial sinks or through ocean fertilization.

7.1.2 Potential Chemical Approaches to Sequestration

One potential approach to sequestration is to transform CO₂ into non-commercial materials that are inert and long-lived, such as magnesium carbonate (MgCO₃). Because they have no commercial value, such materials would need to be sequestered in a relatively inexpensive way, such as refilling the mining pits that first provided the magnesium and associated material. After being incorporated in MgCO₃, the whole world's 1990 output of carbon could be contained in a space 10 km × 10 km × 150 m (see sidebar "The Volume of Carbon Sequestration").

The ocean also may provide an inexpensive site for sequestration of carbon. Carbon dioxide can be incorporated in an ice-like material, called CO₂ clathrate, that is long-lived when located at a sufficient depth below the ocean surface. After being incorporated in CO₂ clathrate, the whole world's 1990 output of carbon could be contained in a space with a volume of approximately 80 km³.

Carbon dioxide, CO, or carbon from energy production also could be recovered and transformed into commercial products (e.g., plastics and rubber) that are inert and long-lived. In 1996, the world's total output of all such products required approximately 206 × 10⁶ tonnes of carbon or 3.5% of the anthropogenic carbon emitted during that year (SRI 1997). Alternately, bulk commodities for use

The Volume Required for Mineral Sequestration



The aerial photograph shows the Bingham Canyon copper mine on the left-hand side. The town of Copperton, Utah, is located to the right of the mine and to the left of the identification number 242 along the top (1 in. = 1.08 miles). Kennecott Copper extracts some 250,000 tons of rock every day from this mine. Kennecott has been mining this deposit for 90 years. The pit is currently half a mile deep and 2.5 miles wide. If it were a stadium, it could seat nine million people. An average sized power plant, operating at 33% efficiency when firing 12,500 Btu/lb coal, would require approximately 35,000 tons of silicate rock per day to capture the CO₂ produced based on the carbonate reaction shown in Table 7.1. To sequester a full year's carbon emissions—based on typical unit availability and capacity factors—would require space equivalent to 35 days of production from this mine.

Comparison Between the Road Map Goal and Large Industrial Activities

A comparison of the amount of material in sequestered carbon and other large earthmoving activities

- The stated goal of this report is to have the capacity to sequester gigatonnes of carbon by the middle of the next century.
- In 1996, U.S. mines shipped approximately 1 gigatonne of sand and gravel.
- In 1996, U.S. mines shipped approximately 1 gigatonne of coal.
- The Iron and Steel Bureau estimates that the productive capacity of the world steel industry is 1 gigatonne per year.
- According to the Chemical Economics Handbook, the world petrochemical industry bases all of its products on seven precursors. Combined, in 1996 these seven precursors embodied approximately 0.2 gigatonnes of carbon.

Table 7.1 Thermodynamics of chemical/physical transformations involving CO₂

Chemical/physical transformation		$\Delta H_{298^\circ\text{K}}$ (Kcal/mole)
<i>Energy production</i>		
Coal combustion	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	-94.05 ^a
Natural gas combustion	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-191.76 ^a
<i>Sequestration</i>		
Bicarbonate	$\text{CO}_2 + 1/2\text{CaSiO}_3 + 1/2\text{H}_2\text{O} \rightarrow 1/2\text{Ca}^{2+} + \text{HCO}_3^- + 1/2\text{SiO}_2$	-15.70 ^a
Carbonate	$\text{CO}_2 + 1/3\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow \text{MgCO}_3 + 2/3\text{SiO}_2 + 2/3\text{H}_2\text{O}$	-3.45 ^a
Oxalate	$\text{CO}_2 + \text{CO} + \text{CaSiO}_3 \rightarrow \text{CaC}_2\text{O}_4 + \text{SiO}_2$	-31.34 ^a
Clathrate	$\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{CO}_2 \cdot 6\text{H}_2\text{O}$	-5.68 ^(at 121°K) ^b
Liquification	$\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{l})$	-1.27 ^(at 298°K, 63.5atm) ^c
<i>Utilization</i>		
Methanol synthesis	$\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-31.30 ^a
(Hydrogen production)	$(3\text{H}_2\text{O} \rightarrow 3\text{H}_2 + 3/2\text{O}_2)$	(+205.05) ^a
Cyclic organic carbonate	$\text{CO}_2 \pm \text{PhCH}=\text{CH}_2 \pm 1/2\text{O}_2 \rightarrow \text{PhCHO}(\text{C}=\text{O})\text{OCH}_2$	-55.3 ^d

^aR. C. Weast, M. J. Astle, and W. H. Beyer. *CRC Handbook of Chemistry and Physics*. CRC Press, Boca Roton, Fla., 1988–1989.

^bS. L. Miller and W. D. Smythe. "Carbon Dioxide Clathrate in the Martian Ice Cap," *Science*, 170 (1970): 531–532.

^cW. M. Braker and L. Allen. *Matheson Gas Data Book*, 6th Ed. Matheson, Lyndhurst, N.J., 1980, p. 26.

^dN. Cohen and S. W. Benson. *Chem. Rev.* 93 (1993):2419–38.

in construction, for example, may represent larger target markets (see the sidebar on potential of sequestration sites and technologies).

In addition, as detailed knowledge is developed, the demands of various sequestration methods may drive the creation of techniques to capture the essence of natural processes. For example, it has been suggested that CO₂ could be sequestered in coal seams. Some of the research needed to investigate that possibility also will bear upon the potential for absorbing CO₂ into other materials that could provide temporary storage; such materials might be used to recover CO₂ from automobile exhaust or directly from the atmosphere. As another example, knowledge of biomimetic chemical techniques—which are essentially models or abstractions of biological processes—might allow us to duplicate these processes under controlled conditions and improve them to enhance reaction rates or

reduce the creation of unwanted or hazardous by-products.

7.2 CHEMICAL PROCESSES FOR SEQUESTRATION

Carbon chemistry is very flexible and has helped to create an impressive array of products. Many chemical process options exist for capture and sequestration or reuse of carbon. However, some require as much energy or consume as much raw material as did the original process that emitted the carbon. Such options may have value in a particular niche market, but they are unlikely to represent significant options for long-term sequestration of large quantities of carbon. Whether a process represents a desirable option varies with the economic circumstances and with the attitudes of society; thus it is important to identify a number of approaches that offer a flexible mix of

options. Options selected must meet these criteria:

- A process must be environmentally benign.
- It must be stable and sustainable for long-duration storage or disposal.
- It must be safe.
- It must be cost-competitive with alternative approaches to sequestration or avoidance.
- Sufficient knowledge of the process, such as thermodynamics and kinetics, must be developed to allow comprehensive analysis.
- It must be *prima facie* reasonable, particularly in terms of the energy balance.

This chapter identifies two groups of chemical processes: (1) those that produce materials for sequestration and (2) those that yield useful products of potential commercial value. We examined the knowledge required to determine whether these concepts represent viable options. We also evaluated the current state of knowledge for each process. For each concept, significant R&D needs included (1) an understanding of the basic chemistry and chemical engineering requirements; (2) process development, optimization, scale-up, and environmental control; and (3) systems issues of environmental and ecological impact and economic acceptability. In most cases, the basic chemical reactions have been identified, the basic thermochemical properties have been tabulated, and some process concepts have been established. However, substantial gaps remain.

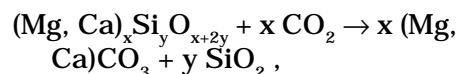
7.2.1 Inert Benign Long-Term Storage Forms

One goal of this effort is to design chemistry-based processes that can

convert separated and captured CO₂ to products appropriate for long-term, environmentally acceptable, and unmonitored storage. It is essential that these options be economically competitive with other approaches to sequestration when performed on the massive scale required to make a significant impact compared with CO₂ production rates. This approach is based on mimicry of natural chemical transformations of CO₂, such as weathering of rocks to form calcium or magnesium carbonates and the dissolution of CO₂ in seawater to yield bicarbonate ions. These two exothermic reactions occur spontaneously in nature. Examples of products for disposal include carbonate (CaCO₃/MgCO₃), bicarbonate (HCO₃⁻), clathrate (CO₂•nH₂O), and oxalate (CaC₂O₄/MgC₂O₄). Table 7.1 presents data on key chemical reactions—some at the heart of the concepts discussed in this section and others that serve as points of reference. Note that schemes to produce fuels, such as methanol, require hydrogen gas. Combining the methanol synthesis reaction and the hydrogen production reaction shows that the combined process would require a large net energy input.

Four possible approaches to these process are discussed and the knowledge gaps are presented for each.

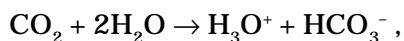
1. The conversion of natural silicate minerals by CO₂ to produce geologically stable carbonate minerals and silica,



is thermodynamically favorable, as is demonstrated by the natural weathering of silicates, albeit at a geologic pace. Current knowledge

of this reaction indicates that it is exothermic, that it can be carried out in several steps, and that sufficient raw materials are available to supply the silicates needed. The challenge is to design conditions of temperature, reaction medium, and reactor configuration that will allow this transformation to be carried out at sufficiently rapid rates. Examples of current studies include direct carbonation of mineral silicates with supercritical CO₂ and water, molten salt carbonation of mineral silicates with molten MgCl₂, and the basic reaction mechanisms of MgOH conversion to MgCO₃. Topics requiring study include (1) the mechanism and kinetics for this gas-solid reaction, as well as catalysts and/or reaction media to promote it; (2) thermodynamics and kinetics of the gas-molten salt reactions and the chloride chemistry; (3) designs for solids-consuming, solids-producing reactors, control of the physical form of the solid products to optimize processing, and corrosion control; and (4) the economic and environmental impacts of mining of the silicates, surface disposal of the carbonate/silica product, and the trace metal products that may offer collateral economic benefits.

2. A second chemical system is dissolution of CO₂ in the oceans (or other natural waters) as soluble bicarbonate,



coupled with the need for a source of added alkali to avoid lowering the pH of the body of water. This pathway is important both for sequestration in geologic

formations and for ocean disposal. The CO₂ might simply be put in the ocean, where most of it would persist as dissolved gas, carbonic acid, and the bicarbonate ion if the CO₂ were injected far enough below the surface. The bicarbonate ion might be created through development of biomimetic pathways in man-made systems and disposed of near the shore in shallow waters, assuming the needed cations could be provided. The current level of understanding of the process of dissolution and reaction is inadequate to allow development of a process with the potential to sequester CO₂ at the rate at which it is currently produced in power plants. R&D on using bicarbonate to sequester CO₂ should address (1) ocean and fresh water and electrolyte chemistry, the influence of solid surfaces, and the precipitation of carbonates; (2) design of reactors and injectors to facilitate efficient mixing of reactants; (3) the effects of enhanced bicarbonate levels on aquatic life and ecology and on the formation of carbonate deposits by advanced biological approaches; (4) rates of transportation from the atmosphere to the ocean; (5) rates of stimulated growth of candidate organisms to capture and hold CO₂; and (6) biomimetic pathways to form calcium carbonate, including the process to make the necessary calcium available to the reaction.

3. The clathrate of CO₂ and H₂O (see Fig. 7.1), structurally analogous to the better known methane hydrate, may offer potential as a form for large-scale storage in the cold oceans or in man-made systems that mimic the requisite conditions. Clathrates may be used in CO₂ separation from high-pressure

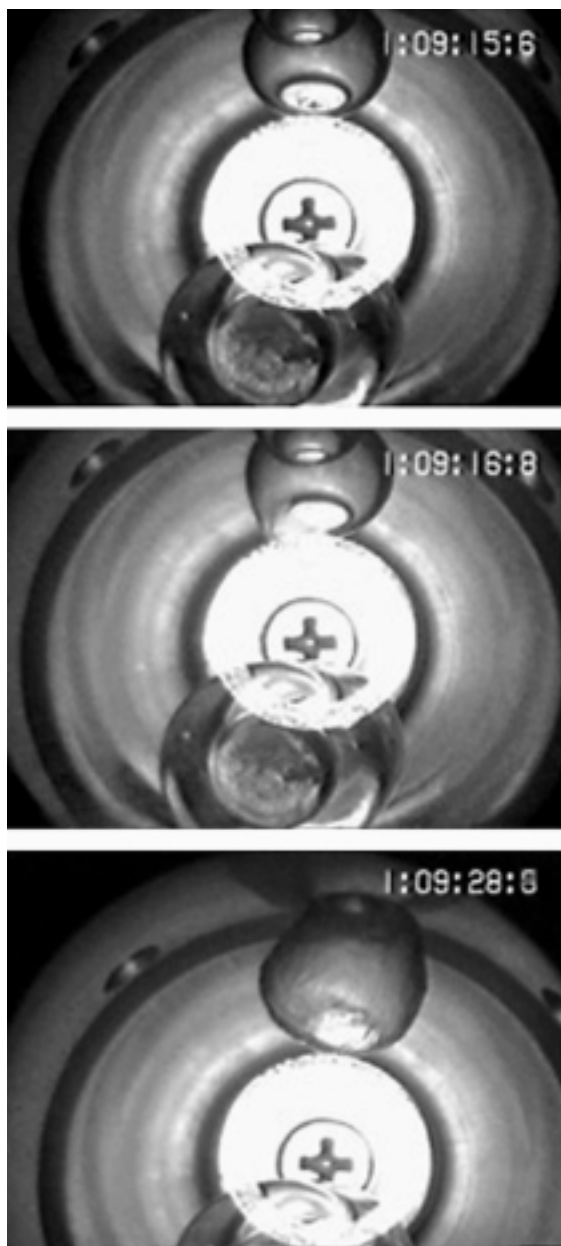


Fig. 7.1. Mixtures of gas clathrates have been found near coasts around the world. These gas hydrates may be mixtures of methane clathrates and CO_2 clathrates. If so, their presence prompts further investigation of the possibility that CO_2 clathrates could be sequestered in the same places. The photos show the formation of a gas clathrate during an experiment.

systems, and their properties may be important to understanding both approaches to ocean disposal and geologic disposal options. Forming

clathrates as a separation step in an integrated gasification combined cycle power plant could be attractive. Preliminary estimates of the energy required indicate that 3 to 4% of the total plant energy would be needed. This is an improvement over techniques available today. Based on what is now known, additional R&D will be required to (1) improve the definition of the phase diagram, thermodynamics, and physical properties of the CO_2 - H_2O system at high pressure in the presence of the electrolytes and impurities found in the ocean, as well as improve the definition of the kinetics of formation and long-term stability of the clathrates; (2) identify practical methods for deep-ocean injection and mixing; and (3) assess the local ecological impacts of hydrate formation. Further exploration would be necessary to determine whether, in the longer term, CO_2 disposal via clathrate formation could be coupled with recovery of methane fuel from the methane hydrate deposits in the oceans.

4. In addition to these process concepts, exploratory R&D is warranted on defining additional low-energy disposal states of carbon that would meet the guiding principles for this topic; examples might include formates and oxalates. Because CO_2 is an acidic gas, it can be captured by using an alkaline substance to form stable compounds with it. A procedure that uses one mole of alkali to transform two moles of CO_2 —such as in the transformation of CO_2 to low-energy-state poly-carbon compounds such as calcium/magnesium oxalate (CaC_2O_4 / MgC_2O_4)—is desirable because of the greater CO_2 -to-alkaline ratio.

Research needs include (1) development of methods for synthesis of regenerable alkaline compounds and for effective use of alkaline; (2) use of molecular modeling to identify new compounds in which one mole of an alkaline species would tie up several moles of CO_2 (Zeissel 1998); (3) exploration of total energy requirements—which include those for chemical reactions as well as those for chemical processing—for both exothermic reactions involving CO_2 and endothermic reactions requiring a small amount of enthalpy input; (4) research into catalysis reactions, process optimization, surface disposal issues, and environmental concerns. Finally, engineering studies and system evaluations of the types described would be needed.

7.2.2 Products from Carbon Dioxide Utilization

The goal of CO_2 utilization is to design chemical processes that can convert separated and captured CO_2 to useful and durable products that have reasonable lifetimes (tens to hundreds of years). Carbon dioxide either in whole or in part can participate in many chemical reactions (Fig. 7.2).

Such utilization strategies, when examined from the perspectives of the current petrochemical industry, will not have the capacity to handle the bulk of emitted CO_2 . However, the products and durable goods that are produced may have greater value and storage lifetimes and lesser environmental impacts than existing means to produce these same products. Additional markets might be developed if R&D were directed toward creation of products with large annual uses, such

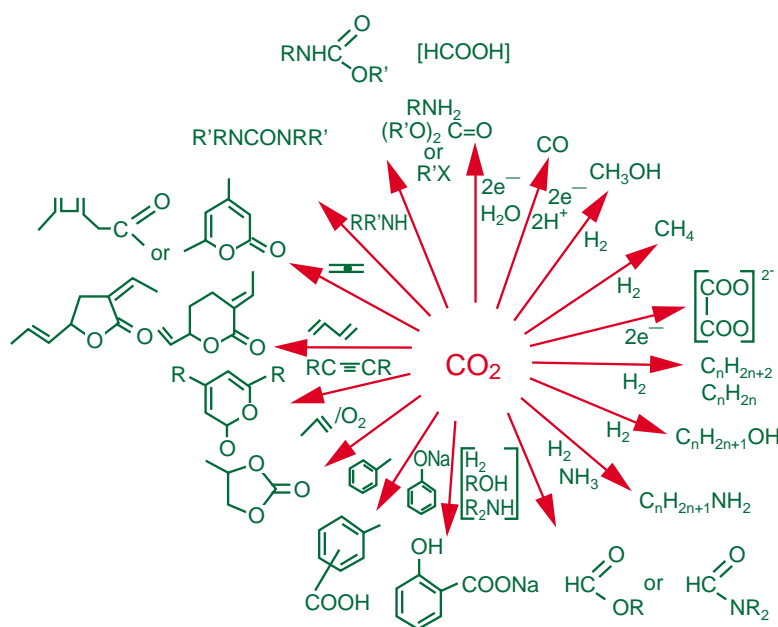


Fig. 7.2. Paths to utilize CO_2 in synthetic chemistry. Source: Aresta 1998.

Use of Carbon in Ultralight Vehicles

The Rocky Mountain Institute has performed a number of analyses on development of ultralight vehicles. In December 1996, it published a report titled "Costing the Ultralite in Volume Production: Can Advanced-Composite Bodies-in-White be Affordable?" (Mascarin et al. 1996) that examines the use of a carbon-fiber-composite monocoque body-in-white in an ultralight vehicle or hypercar. The body of the car would be made of parts molded from advanced polymer composites and assembled with adhesives. The composites could be formed from carbon fibers embedded in an epoxy or other resin. The carbon fibers could represent approximately 50% of the total weight.

The typical hypercar prepared from these materials would have a curb weight of 637 kg, of which approximately 190 kg is the weight of the monocoque body. If carbon from the fuel cycle were used to create the products needed for construction of such a vehicle, each body shell might contain 100–150 kg of carbon (the report does not list the actual percentage of carbon in the monocoque body). The report discusses the cost of carbon fiber in terms of the size of the market needed to ensure a low cost for the needed material—a market of approximately 0.6 to 0.9 million carbon-fiber cars per year.

Assume that all the needed carbon from such a car body could be derived from either fuel decarbonization or from products made from CO or CO₂ captured after some or all of the chemical energy had been used for energy production. Then this market might require carbon sufficient to make approximately 750,000 cars/year, each car requiring 125 kilograms of carbon. This usage represents approximately 100,000 tonnes of carbon per year. A total of 750,000 cars per year would represent approximately 10% of the current U.S. new car market.

as construction materials or parts for automobile bodies (see sidebar on use of carbon in ultralight vehicles). However, widespread use of carbon-based products would require large shifts in infrastructure and would face stiff competition from the industries manufacturing the products they sought to displace.

Four end-uses that could be viewed as supporting the need for a particular technology are described in the following paragraphs, and gaps in knowledge are identified. This list is not comprehensive because of the great variety of organic synthesis routes that exist, but it provides a sense of the opportunity and scope of this approach to carbon sequestration. (See also Inui et al. 1998 and ACS et al. 1996).

- Particulate carbon, perhaps from methane decarbonization, could be converted into new composite materials and used in durable construction materials such as concrete. The challenge is finding economically viable methods of converting solid carbon into durable goods and new composites. An associated issue is the physical characteristics of the supplied carbon, assuming that the carbon comes from fuel decarbonization processes. Scientific and technological capabilities are needed to define the chemical pathways from hydrocarbons to solid carbon, discover new composite chemistry, and understand how to incorporate carbon into new building materials.

Specific needs include identification of (1) thermochemical processes, (2) new catalysts and reactors, and (3) alternative fuel sources. The lifetime of the product or material is a key variable to be considered in performing life-cycle and system cost and performance analyses.

- Many studies have addressed the need to identify ways to use CO₂ as a carbon feedstock for production of plastics or other similar commodities. Needed scientific and technological capabilities include (1) definition of chemical reaction pathways, (2) catalyst development, and (3) process development and optimization. A significant environmental driver is the substitution of CO₂ for toxic substances such as phosgene, which is used as a feedstock to produce isocyanates, polycarbonates, and other products used in industrial processes. Research has uncovered the pathway for this substitution to occur exothermically, implying that more benign processing may be an economic driver as well. Product lifetimes need to be assessed, but we assume that they will be on the order of decades to centuries. Another approach might be partial oxidation (via gasification) to produce energy and some CO that could serve as a feedstock for chemical processes.
- Alternately, it might be possible to use the carbon either from the fuel or from products of the combustion process to create soil amendments to enhance sequestering carbon in natural systems. Similar technical concerns exist about, for example, how to optimize these products for their desired end use. However, the

requirements for achieving product purity and for avoiding potential environmental impacts differ.

- Finally, much attention has been focused on carbon-neutral processes in which fuels and chemicals are formed from CO₂ feedstocks via pathways that would use renewable energy sources. Scientific and technological capabilities will be needed to identify new catalysts, electrocatalysts, and efficient reactors. However, this approach requires a source of cheap hydrogen to react with CO₂. Schemes have been proposed to split water to provide a source of hydrogen. Direct use of H₂ as a fuel, as an alternative to reacting hydrogen with CO₂, should be addressed through a systems evaluation of costs and benefits. In general, the question of sequestration or avoidance needs to be addressed with respect to carbon-neutral processing.

7.3 ENABLING CHEMICAL TECHNOLOGIES

Previous sections of this chapter described the chemical aspects of sequestering CO₂ for ocean storage of bicarbonates and clathrates; land storage as solid alkaline carbonates; cross-compounds in which a simple cation ties up a number of CO₂ molecules; and storage in durable materials such as plastics, composites, and chemicals. Significant developments in enabling science and associated technologies are needed to support these concepts (see Fig. 7.3). Some processes will be greatly aided by improving computational capabilities related to molecular modeling for novel synthesis routes to make carbon-

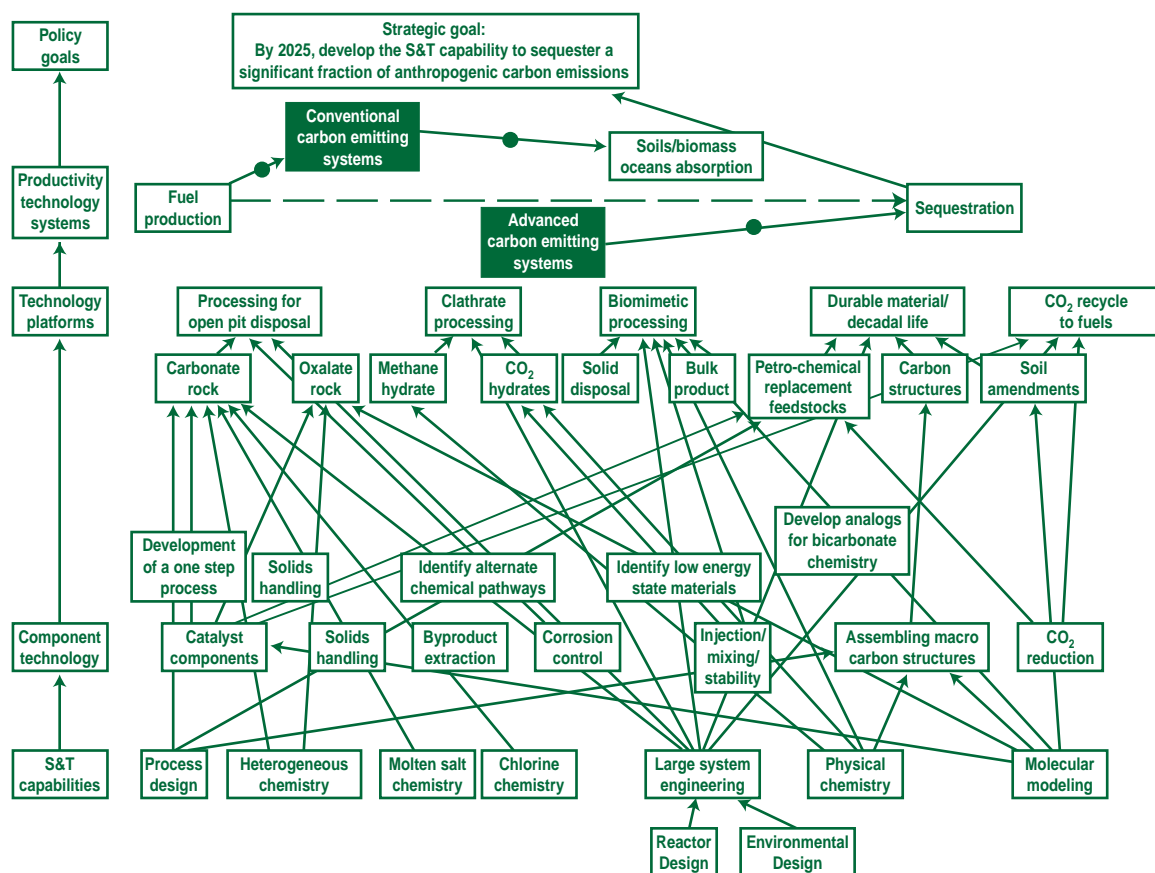


Fig 7.3. A road map of needed research into advanced chemical approaches. The science and technology capabilities address needs of both advanced chemical processes and the other focus areas. These capabilities are topics that need attention in the near term, as are the component technologies that support the carbonate rock option and biomimetic processing (the latter would enhance the chances for success of sequestration in oceans and geologic formations).

based products, or for development of improved solvents such as sterically hindered amines to capture carbon from flue gases. Many of these capabilities are already under development to support creation of new energy and environmental technologies. A partial list of the enabling technologies needed includes

- Develop catalysts needed to enhance geologic sequestration, use of the carbon in CO_2 , and decarbonization (e.g., mimic photosynthesis; use TiO_2 and sunlight to split CO_2)
- Develop new solvents and sorbents for gas separations (O_2 from air or CO_2 from flue gas)
- Develop a thorough understanding of the chemistry key to CO_2 adsorption and methane desorption from coal seams
- Explore novel formulations for fertilizers to be applied to enhance terrestrial or oceanic sequestration concepts
- Create membranes and thin films for advanced separations (e.g., high-temperature ceramic membranes to enable air separation)
- Develop agglomerating agents, binding agents (e.g., coal and lithium zirconate), and coatings

- Improve high-temperature materials, particularly metal oxides (e.g., BaO and BaO₃ cycles for high-temperature separation or NiO or CoO mixed with yttria-stabilized zirconia for chemical looping combustion)
- Explore novel reactor concepts and the requisite sensors and controls

The development of improved catalysts and other new materials is particularly important.

Catalysis. Developing effective catalysts capable of multiple electron reduction chemistry is the major challenge for creating an effective technology for reducing CO₂ to high-energy intermediates. Considerable success has been achieved in the design, synthesis, and analyses of donor and acceptor assemblies capable of light-driven, one-electron charge separation processes. Current research demonstrates that remarkably enhanced catalytic efficiencies are achieved in natural and artificial photochemical systems by inducing redox chemistry on surfaces in constrained, structured environments.

Novel structured catalytic assemblies capable of initiating single-step, multiple-electron, reductive chemistry are needed. Redox assemblies capable of cooperative charge accumulation mimic the biological process of CO₂ reduction in photosynthesis and would provide a photoelectrochemical system that could use CO₂ as a chemical feedstock for synthesis of carbon-based chemicals.

New catalysts will be required to enhance the rates of formation of alkaline carbonates and oxalates. Additives that could enhance geologic sequestration of CO₂ also are needed.

These materials would be injected with CO₂ early in the period of use to coat the cap rock or features toward the boundary of the reservoir. Over time, say after 5 years, they would begin to react with the injected CO₂ to seal the reservoir and reduce the potential for leakage.

New materials. New materials are needed to handle the extreme process conditions of molten salt chemistry. Chemical approaches (e.g., barium oxide and barium peroxide) to air separation or chemical looping combustion (nickel oxide or cobalt oxide mixed with yttria-stabilized zirconia) should be studied because they can take advantage of the high temperatures available at power plants. Binding and agglomeration processes must be defined both for the fabrication of products from particulate carbon and for other uses, such as the capture of CO₂ from vehicles. For example, materials like lithium zirconate might be good CO₂ absorbers and thus enable the capture of some CO₂ from vehicle emissions, a hitherto overlooked approach that merits long-range, high-risk research. As another example, composite materials that might result from adding carbon to plastics, polymers, glasses, cements and ceramics should be studied.

7.4 SUMMARY

This chapter explored three approaches to carbon sequestration using advanced chemical technologies:

1. Develop benign by-products for disposal. This avenue may offer the potential to sequester large (gigatonne) amounts of anthropogenic carbon.

2. Produce commercial products. This topic probably represents a lesser potential (millions of tonnes) but may result in collateral benefits tied to pollution prevention.
3. Conduct enabling studies that may impact the ability of technologies under development in other focus areas to meet their potential.

Based on our review of advanced chemical concepts, and recognizing needs identified in other focus areas, priority should be placed on obtaining the chemical knowledge required to

- Absorb/adsorb CO_2 in coal seams.
- Create MgCO_3 as described in the carbonate reaction in Table 7.1. The product is inert and benign.
- Understand and exploit CO_2 clathrates, ice-like materials that precipitate out of mixtures of water and CO_2 under the proper conditions.
- Form and dispose of aqueous solutions of carbonates, the bicarbonate ion being the most prominent, in the ocean or other appropriate bodies of water.
- Develop commercial products made from CO_2 , CO (from advanced power system concepts), or carbon created via decarbonization.

Table 7.2 provides more information about these approaches.

The materials above the double line (that is, oxalates, etc.) have virtually unlimited carbon sequestration potential. The ones below the line are less likely to play a major role based on both thermodynamic considerations and the potential size of target markets. Given current consumption patterns, only a small percentage of fossil carbon feedstocks is used for producing carbon-based goods. The rest goes toward energy production. Reduced carbon will be of interest in niche markets that are driven by the value of the products they generate. The chemical industry could use new chemical processes for producing valuable chemicals and materials, as well as avoid potential environmental penalties for continued CO_2 emissions. The economic benefits of new processes might provide increased technological competitiveness for industry and the ability to use CO_2 as a feedstock for chemical production in addition to current petroleum-based feedstocks. However, the overall effect of product development on carbon sequestration is likely to be small unless new products that are used in large quantities can be developed, such as building materials or materials

Table 7.2 Approaches to sequestration using chemical processes and examples of their use

Chemical form of carbon	Examples of implementation
Aqueous carbonate ions: CO_3^{--} , HCO_3^- Solid carbonates: CaCO_3 , MgCO_3	Ocean disposal, deep saline aquifers Terrestrial, ocean floor, underground disposal
Clathrates: $\text{CO}_2 \cdot n\text{H}_2\text{O}$, $n \sim 6$ Carbon adsorption of CO_2 Other low-energy states of carbon, such as oxalates	Ocean, ocean floor disposal Coal bed methane extraction Novel disposal technologies
Solid carbon	Underground disposal, feedstock for composite materials
Carbon-based fuels (e.g., methanol) Carbon bound in durable commercial goods (e.g., plastics)	CO_2 -based fuel cycles, alternative energy Long-lived construction materials

for automobile bodies. Based on the scale of sequestration that may be needed, our analysis favors research into those chemical options that offer the greater sequestration potential. Thus we consider stable and benign end products for disposal a more promising approach to the problem. In addition, enabling studies should be pursued that benefit both other sequestration methods and the development of chemical means to mimic natural processes under controlled conditions.

7.5 END NOTES

1. In hydrate-clathrate, the maximum ratio of guest molecules (e.g., CO_2) to water molecules is approximately 1/7. (See E. Denude Sloan, Jr., 1998. *Clathrate Hydrates of Natural Gases*, Marcel Dekker, New York, p. 53.) The density of ice is approximately 0.9 grams/cm³. To establish the needed order of magnitude, we assume that one gram-mole of ice (18 grams) occupies 20 cm³ and that at most 1/7 gram-mole of CO_2 (44/7 grams) occupies the same 20 cm³. Thus 1/7 gram-mole of carbon occupies at least 20 cm³, probably more. Hence we estimate the maximum effective density to be 12/7 grams of carbon per 20 cm³, which is 0.085 grams carbon per cm³. Thus after 10⁹ tonnes of carbon was incorporated in CO_2 clathrate, this clathrate would occupy a volume of at least 1.2 × 10¹¹ m³ or 12 km³.
2. The ratio of the mass of MgCO_3 to the mass of carbon incorporated therein is 7. It follows that 10⁹ tonnes of carbon would be bound within 7 × 10⁹ tonnes of MgCO_3 . The density of crystalline

MgCO_3 is 3 grams/cm³. In practice, powdered material with a bulk density of somewhat less would be sequestered. Perhaps about 10% more space would be needed for powder than for crystal (e.g., 2.7 grams/cm³). If so, 7 × 10⁹ tonnes of MgCO_3 would occupy 2.6 × 10⁹ m³, which is the volume of a box whose sides are 10 km by 10 km and whose height is 26 m.

7.6 REFERENCES

- ACS (American Chemical Society), American Institute of Chemical Engineers, Chemical Manufacturers Association, Council for Chemical Research, and Synthetic Organic Chemical Manufacturers Association 1996. *Technology Vision 2020: The U.S. Chemical Industry*, Washington, D.C., available at <http://www.chem.purdue.edu/ccr/v2020/> (accessed 12/21/98).
- Aresta, Michele 1998. "Perspectives of Carbon Dioxide Utilization in the Synthesis of Chemicals. Coupling Chemistry with Biotechnology," in T. Inui, M. Anpo, K Izui, S. Yanagida, T. Yamaguchi, eds., *Advances in Chemical Conversions for Mitigating Carbon Dioxide: Proceedings of the Fourth International Conference on Carbon Dioxide Utilization, Kyoto, Japan, September 7-11, 1997*, Vol. 114, Elsevier Science B.V.
- EIA (Energy Information Administration) 1997. *Emissions of Greenhouse Gases in the United States 1996*, DOE/EIA-0573, U.S. Department of Energy, Washington, D.C., October.
- EIA (Energy Information Administration) 1998. *International Energy Outlook, 1998*, DOE/EIA-0484, Washington, D.C., April.

- Inui, T., M. Anpo, K Izui, S. Yanagida, T. Yamaguchi, eds. 1998. *Advances in Chemical Conversions for Mitigating Carbon Dioxide: Proceedings of the Fourth International Conference on Carbon Dioxide Utilization*, Kyoto, Japan, September 7–11, 1997, Vol. 114, Elsevier Science B.V.
- Mascarin, A. E., J. R. Dieffenbach, M. M. Brylawski, D. R. Cramer, and A. B. Lovins 1996. *Costing the Ultralight in Volume Production: Can Advanced-Composite Bodies-in-White be Affordable?* (December 1996 revision), available at http://www.rmi.org/hypercars/b_i_w/T95_35.html (accessed 12/21/98).
- SRI International 1997. *The Chemical Economics Handbook*, Menlo Park, Calif., 350.0000E.
- Zeissel, R. 1998. "Molecular Tailoring of Organometallic Polymers for Efficient Catalytic CO₂ Reduction: Mode of Formation of Active Species," in T. Inui, M. Anpo, K. Izui, S. Yanagida, T. Yamaguchi, eds., *Advances in Chemical Conversions for Mitigating Carbon Dioxide: Proceedings of the Fourth International Conference on Carbon Dioxide Utilization*, Kyoto, Japan, September 7–11, 1997, Vol. 114, Elsevier Science B.V.

